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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 1/825, 1/83, 1/94	A1	(11) International Publication Number: WO 95/23204 (43) International Publication Date: 31 August 1995 (31.08.95)
(21) International Application Number: PCT/US95/02162 (22) International Filing Date: 27 February 1995 (27.02.95) (30) Priority Data: 08/203,125 28 February 1994 (28.02.94) US 08/384,310 6 February 1995 (06.02.95) US (71) Applicant: COLGATE-PALMOLIVE COMPANY [US/US]; 300 Park Avenue, New York, NY 10022 (US). (72) Inventors: ERILLI, Rita; Avenue de Voroux 25, B-4000 Ro- court (BE). ADAMY, Steven; 12 Brown Drive, Hamilton, NJ 08690 (US). MEHRETEAB, Ammanuel; 6 Thornton Lane, Piscataway, NJ 08854 (US). BALA, Frank, Jr.; 405 1st Street, Middlesex, NJ 08846 (US). (74) Agent: NANFELDT, Richard, E.; Colgate-Palmolive Com- pany, 909 River Road, Piscataway, NJ 08855-1343 (US).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: LIQUID DETERGENT (57) Abstract A high foaming, light duty, liquid detergent with desirable cleansing properties and mildness to the human skin comprising a partially esterified ethoxylated polyhydric alcohol and at least one surfactant selected from the group consisting of a water-soluble nonionic surfactant, at least one water-soluble, foaming, anionic surfactant and a water-soluble, foaming zwitterionic betaine surfactant.		

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LIQUID DETERGENT

Background of the Invention

The present invention relates to novel light duty liquid detergent compositions with high foaming properties, containing a nonionic surfactant and/or anionic surfactants, an esterified polyethoxy ether nonionic surfactant, and optionally a zwitterionic betaine surfactant, wherein the surfactants are dissolved in an aqueous medium.

Nonionic surfactants are in general chemically inert and stable toward pH change and are therefore well suited for mixing and formulation with other materials. The superior performance of nonionic surfactants on the removal of oily soil is well recognized. Nonionic surfactants are also known to be mild to human skin. However, as a class, nonionic surfactants are known to be low or moderate foamers. Consequently, for detergents which require copious and stable foam, the application of nonionic surfactants is limited. There have been substantial interest and efforts to develop a high foaming detergent with nonionic surfactants as the major ingredient. Little has been achieved.

The prior art is replete with light duty liquid detergent compositions containing nonionic surfactants in combination with anionic and/or betaine surfactants wherein the nonionic detergent is not the major active surfactant, as shown in U.S. Patent No. 3,658,985 wherein an anionic based shampoo contains a minor amount of a fatty acid alkanolamide. U.S. Patent No. 3,769,398 discloses a betaine-based shampoo containing minor amounts of nonionic surfactants. This patent states that the low foaming properties of nonionic detergents renders its use in shampoo compositions non-preferred. U.S. Patent No. 4,329,335 also discloses a shampoo containing a betaine surfactant as the major ingredient and minor amounts of a nonionic surfactant and of a fatty acid mono- or di-ethanolamide. U.S. Patent No. 4,259,204 discloses a shampoo comprising 0.8-20% by weight of an anionic phosphoric acid ester and one additional surfactant which may be either anionic, amphoteric, or nonionic. U.S.

Patent No. 4,329,334 discloses an anionic-amphoteric based shampoo containing a major amount of anionic surfactant and lesser amounts of a betaine and nonionic surfactants.

U.S. Patent No. 3,935,129 discloses a liquid cleaning composition based on the alkali metal silicate content and containing five basic ingredients, namely, urea, glycerin, triethanolamine, an anionic detergent and a nonionic detergent. The silicate content determines the amount of anionic and/or nonionic detergent in the liquid cleaning composition. However, the foaming property of these detergent compositions is not discussed therein.

U.S. Patent No. 4,129,515 discloses a heavy duty liquid detergent for laundering fabrics comprising a mixture of substantially equal amounts of anionic and nonionic surfactants, alkanolamines and magnesium salts, and, optionally, zwitterionic surfactants as suds modifiers.

U.S. Patent No. 4,224,195 discloses an aqueous detergent composition for laundering socks or stockings comprising a specific group of nonionic detergents, namely, an ethylene oxide of a secondary alcohol, a specific group of anionic detergents, namely, a sulfuric ester salt of an ethylene oxide adduct of a secondary alcohol, and an amphoteric surfactant which may be a betaine, wherein either the anionic or nonionic surfactant may be the major ingredient.

The prior art also discloses detergent compositions containing all nonionic surfactants as shown in U.S. Patent Nos. 4,154,706 and 4,329,336 wherein the shampoo compositions contain a plurality of particular nonionic surfactants in order to effect desirable foaming and deterative properties despite the fact that nonionic surfactants are usually deficient in such properties.

U.S. Patent No. 4,013,787 discloses a piperazine based polymer in conditioning and shampoo compositions which may contain all nonionic surfactant or all anionic surfactant.

U.S. Patent No. 4,450,091 discloses high viscosity shampoo compositions containing a blend of an amphoteric betaine surfactant, a polyoxybutylene

polyoxyethylene nonionic detergent, an anionic surfactant, a fatty acid alkanolamide and a polyoxyalkylene glycol fatty ester.

U.S. Patent No. 4,595,526 describes a composition comprising a nonionic surfactant, a betaine surfactant, an anionic surfactant and a C₁₂-C₁₄ fatty acid
5 monoethanolamide foam stabilizer.

A number of patents teach esterified ethoxylated glycerol compounds for various applications. These patents are Great Britian 1,453,385; Japan 59-1600 and Japan 58-206693 and European Patent Application 0586,323A1. These publications fail to appreciate that a mixture of esterified ethoxylated glycerol and nonesterified
10 ethoxylated glycerol, when used in a hard surface cleaning composition, functions as a grease release agent.

However, none of the above-cited patents discloses a high foaming, liquid detergent composition containing a nonionic surfactant and/or anionic surfactants, a solubilizing agent which is a partially esterified ethoxylated polyhydric alcohol, and
15 optionally a foaming zwitterionic surfactant selected from betaine type surfactants, wherein the composition does not contain any amine oxide, calcium carbonate, polymeric or clay thickeners, abrasives, clays, silicas, alkyl glycine surfactant, cyclic imidinium surfactant, or more than 3.0 wt. % of a fatty acid or a metal salt of the fatty acid compounds.

20 Summary of the Invention

It has now been found that a high foaming liquid detergent can be formulated with a partially esterified ethoxylated polyhydric alcohol which has desirable cleaning properties, mildness to the human skin.

Another object of this invention is to provide novel, liquid aqueous detergent
25 compositions containing a nonionic surfactant and/or anionic surfactants, a partially esterified ethoxylated polyhydric alcohol, and optionally a zwitterionic betaine surfactant, wherein the composition does not contain amine oxide, an alkali metal carbonate, polymeric or clay thickeners, clays, abrasives, alkyl glycine surfactants,

cyclic imidinium surfactants, silicas or more than 3 wt. % of a fatty acid or a metal salt of a fatty acid.

Still another object of this invention is to provide a novel, liquid detergent with desirable high foaming and cleaning properties which is mild to the human skin.

5 Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in
10 the appended claims.

More specifically, the present invention relates to a high foaming liquid detergent comprising: a nonionic surfactant selected from the group consisting of water soluble primary aliphatic alcohol ethoxylates secondary aliphatic alcohol ethoxylates, alkyl phenol ethoxylates and alcohol ethylene oxide propylene oxide
15 condensates, and/or at least one anionic surfactant selected from the group consisting of water soluble salts of C₈-C₁₈ alkyl sulfates, C₈-C₁₆ benzene sulfonates, C₁₀-C₂₀ paraffin sulfonates, C₈-18 ethoxylated alkyl ether sulfate; alpha C₁₀-C₂₄ olefin sulfonates, C₈-C₁₈ alkyl sulfoacetates, C₈-C₁₈ alkyl sulfosuccinate esters, C₈-C₁₈ acyl isethionates and C₈-C₁₈ acyl taurates, a partially esterified ethoxylated
20 polyhydric alcohol, and optionally a water soluble zwitterionic betaine surfactant, wherein the surfactants are dissolved in an aqueous vehicle.

Detailed Description of the Invention

The high foaming light duty liquid detergent compositions of the instant invention comprise approximately by weight: 0 to 30 wt. % of a water soluble nonionic
25 surfactant; 0 to 40 wt. % of at least one water soluble or dispersible anionic surfactant; 1 to 23% of a solubilizing agent which is an esterified ethoxylated polyhydric alcohol such as partially esterified ethoxylated glycerol; 0 to 10.0 wt. % of a betaine surfactant; and 44 to 90 wt. % of water, wherein the compositions do not contain any amine oxides, calcium carbonate, polymeric or clay thickeners, abrasives, clays, silicas, alkyl

glycine surfactants, cyclic imidinium surfactants, or more than 3 wt. % of a fatty acid or a metal salt of the fatty acid.

The nonionic surfactant can be present in the liquid detergent composition in amounts of 0 to 30%, preferably 1 to 25%, most preferably 2 to 22%, by weight of the composition and provides superior performance in the removal of oily soil and mildness to human skin.

The water soluble nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkylphenol ethoxylates. The nonionic synthetic organic surfactants generally are the condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water soluble nonionic surfactant.

The nonionic surfactant class includes the condensation products of a higher alcohol (e.g., an alkanol containing 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with 16 moles of ethylene oxide (EO), tridecanol condensed with 6 to moles of EO, myristyl alcohol condensed with 10 moles of EO per mole of myristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms in length and wherein the condensate contains either 6 moles of EO per mole of total alcohol or 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing 9-15 carbon atoms, such as C₉-C₁₁ alkanol condensed with 8 moles of ethylene oxide (Neodol 91-8), C₁₂-C₁₃ alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-

6.5), C₁₂₋₁₅ alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C₁₄₋₁₅ alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrophilic / lipophilic balance) value of 8 to 15 and give good O/W emulsification, whereas ethoxamers with HLB values below 8 contain
5 less than 5 ethyleneoxide groups and tend to be poor emulsifiers and poor detergents.

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of
10 ethylene oxide. Examples of commercially available nonionic detergents of the foregoing type are C₁₁-C₁₅ secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

Other suitable nonionic surfactants include the polyethylene oxide condensates of one mole of alkyl phenol containing from 8 to 18 carbon atoms in a straight- or
15 branched chain alkyl group with 5 to 30 moles of ethylene oxide. Specific examples of alkyl phenol ethoxylates include nonyl condensed with 9.5 moles of EO per mole of nonyl phenol, dinonyl phenol condensed with 12 moles of EO per mole of phenol, dinonyl phenol condensed with 15 moles of EO per mole of phenol and di-
isooctylphenol condensed with 15 moles of EO per mole of phenol. Commercially
20 available nonionic surfactants of this type include Igepal CO-630 (nonyl phenol ethoxylate) marketed by GAF Corporation.

The at least one anionic surfactant, used in the liquid detergent composition, constitutes 0% to 40%, preferably 1% to 30%, most preferably 1 to 15%, by weight thereof and provides good foaming properties. However, preferably reduced amounts
25 are utilized in order to enhance the mildness of the skin property desired in the inventive compositions.

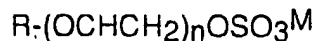
The anionic surfactant which may be used in the liquid detergent of the invention are water soluble such as triethanolamine salt and include the sodium, potassium, ammonium and ethanalammonium salts of C₈₋₁₈ alkyl sulfates such as

lauryl sulfate, myristyl sulfate and the like; ethoxylated C₈-18 alkyl ether sulfates; linear C₈-C₁₆ alkyl benzene sulfonates; C₁₀-C₂₀ paraffin sulfonates; alpha olefin sulfonates containing 10-24 carbon atoms; C₈-C₁₈ alkyl sulfoacetates; C₈-C₁₈ alkyl sulfosuccinate esters; C₈-C₁₈ acyl isethionates; and C₈-C₁₈ acyl taurates. Preferred
5 anionic surfactants are the water soluble C₁₂-C₁₆ alkyl sulfates, the C₁₀-C₁₅ alkylbenzene sulfonates, the C₁₂-C₁₇ paraffin sulfonates and the alpha C₁₂-C₁₈ olefin sulfonates.

The paraffin sulfonates may be monosulfonates or di-sulfonates and usually are mixtures thereof, obtained by sulfonating paraffins of 10 to 20 carbon atoms.
10 Preferred paraffin sulfonates are those of C₁₂-18 carbon atoms chains, and more preferably they are of C₁₄-17 chains. Paraffin sulfonates that have the sulfonate group(s) distributed along the paraffin chain are described in U.S. Patents, 2,503,280; 2,507,088; 3,260,744; and 3,372,188; and also in German Patent 735,096. Such compounds may be made to specifications and desirably the content of paraffin
15 sulfonates outside the C₁₄-17 range will be minor and will be minimized, as will be any contents of di- or poly-sulfonates.

Examples of suitable other sulfonated anionic surfactants are the well known higher alkyl mononuclear aromatic sulfonates, such as the higher alkylbenzene sulfonates containing 9 to 18 or preferably 9 or 10 to 15 or 16 carbon atoms in the
20 higher alkyl group in a straight or branched chain, or C₈-15 alkyl toluene sulfonates. A preferred alkylbenzene sulfonate is a linear alkylbenzene sulfonate having a higher content of 3-phenyl (or higher) isomers and a correspondingly lower content (well below 50%) of 2-phenyl (or lower) isomers, such as those sulfonates wherein the benzene ring is attached mostly at the 3 or higher (for example 4, 5, 6 or 7) position of
25 the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1 position is correspondingly low. Preferred materials are set forth in U.S. Patent 3,320,174, especially those in which the alkyls are of 10 to 13 carbon atoms.

The ethoxylated alkyl ether sulfate which can be used in the instant composition is depicted by the formula:

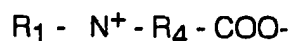


wherein n is 1 to 22 more preferably 1 to 3 and R is an alkyl group having 8 to 18 carbon atoms, more preferably 12 to 15 and natural cuts, for example, C₁₂₋₁₄; C₁₂₋₁₅ and M is a metal cation most preferably sodium or magnesium and n is 1 to 3.

5 The ethoxylated alkyl ether sulfate may be made by sulfating the condensation product of ethylene oxide and C₈₋₁₈ alkanol, and neutralizing the resultant product. The ethoxylated alkyl ether sulfates differ from one another in the number of carbon atoms in the alcohols and in the number of moles of ethylene oxide reacted with one mole of such alcohol. Preferred ethoxylated alkyl ether polyethenoxy sulfates contain
10 12 to 15 carbon atoms in the alcohols and in the alkyl groups thereof, e.g., sodium myristyl (3 EO) sulfate.

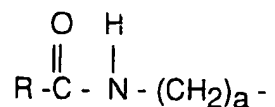
Ethoxylated C₈₋₁₈ alkylphenyl ether sulfates containing from 2 to 6 moles of ethylene oxide in the molecule also are suitable for use in the invention compositions. These detergents can be prepared by reacting an alkyl phenol with 2 to 6 moles of
15 ethylene oxide and sulfating and neutralizing the resultant ethoxylated alkylphenol.

The water-soluble zwitterionic surfactant, which can also present in the liquid detergent composition, constitutes 0 to 10%, preferably 1 to 9%, most preferably 2 to 8%, by weight and provides good foaming properties and mildness to the present nonionic based liquid detergent. The zwitterionic surfactant is a water soluble betaine
20 having the general formula:

$$R_2$$


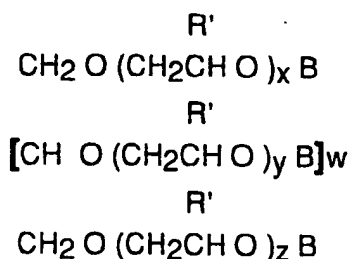
$$R_3$$

25 wherein R₁ is an alkyl group having 10 to 20 carbon atoms, preferably 12 to 16 carbon atoms, or the amido radical:



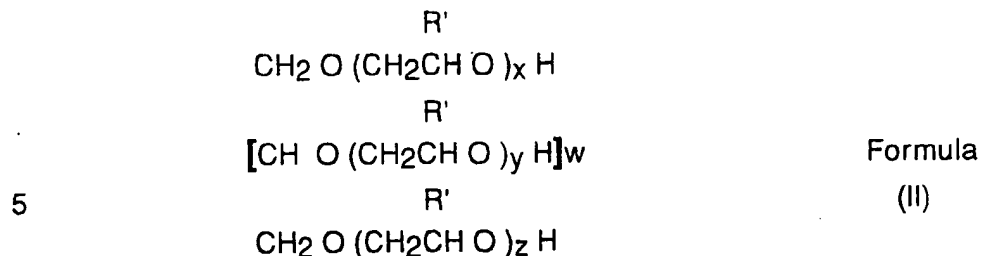
wherein R is an alkyl group having 9 to 19 carbon atoms and a is the integer 1 to 4; R₂ and R₃ are each alkyl groups having 1 to 3 carbons and preferably 1 carbon; R₄ is an alkylene or hydroxyalkylene group having from 1 to 4 carbon atoms and, optionally, one hydroxyl group. Typical alkyldimethyl betaines include decyl dimethyl betaine or 2-(N-decyl-N, N-dimethyl-ammonia) acetate, coco dimethyl betaine or 2-(N-coco N, N-dimethylammonio) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, lauryl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine, etc. The amidobetaines similarly include cocoamidoethylbetaine, cocoamidopropyl betaine and the like. A preferred betaine is coco (C₈-C₁₈) amidopropyl dimethyl betaine. The instant composition contains at least 1 wt. %, more preferably at least 3 wt. %, and most preferably at least 5 wt. % of at least one of the surfactants selected from the group consisting of the nonionic surfactant, the anionic surfactant and the betaine surfactant or a mixture thereof.

The partially esterified ethoxylated polyhydric alcohol such as an ethoxylated glycerol type solubilizing agents of the instant invention are a mixture of nonesterified species, partially esterified species and fully esterified species as depicted by the following Formulas (I) and (II):



Formula
(I)

and

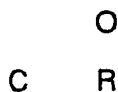


wherein w equals one to four, most preferably one. B is selected from the group consisting of hydrogen or a group represented by:



wherein R is selected from the group consisting of alkyl group having 6 to 22 carbon atoms, more preferably 11 to 15 carbon atoms and alkenyl groups having 6 to 22 carbon atoms, more preferably 11 to 15 carbon atoms, wherein a hydrogenated tallow alkyl chain or a coco alkyl chain is most preferred, wherein at least one of the B

groups is represented by said



and R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, more preferably 0 to 40, provided that (x+y+z) equals 2 to 100, preferably 4 to 24 and most preferably 4 to 19, wherein in Formula (I) the ratio of monoester/diester/triester is 45 to 90/5 to 40/1 to 20, more preferably 50 to 90/9 to 32/1 to 12, wherein the ratio of Formula (I) to Formula (II) is a value between 3 to 0.33, preferably 1.5 to 0.4.

The ethoxylated glycerol type solubilizing agent used in the instant composition are manufactured by the Kao Corporation and sold under the trade name Levenol such as Levenol F-200 which has an average EO of 6 and a molar ratio of coco fatty acid to glycerol of 0.55 or Levenol V501/2 which has an average EO of 17 and a molar ratio of tallow fatty acid to glycerol of 1.0. The ethoxylated glycerol type solubilizing agent has a molecular weight of 400 to 1600, and a pH (50 grams/liter of water) of 5-7. The Levenol solubilizing agents are substantially nonirritant to human skin and have a

primary biodegradability higher than 90% as measured by the Wickbold method Bias-7d.

Two examples of the Levenol solubilizing agents are the Levenol V-501/2 which has 17 ethoxylated groups and is derived from tallow fatty acid with a fatty acid to glycerol ratio of 1.0 and a molecular weight of 1465 and Levenol F-200 has 6
5 ethoxylated groups and is derived from coco fatty acid with a fatty acid to glycerol ratio of 0.55. Both Levenol F-200 and Levenol V-501/2 are composed of a mixture of Formula (I) and Formula (II). The Levenol solubilizing agent have ecotoxicity values of algae growth inhibition > 100 mg/liter; acute toxicity for Daphniae > 100 mg/liter and
10 acute fish toxicity > 100 mg/liter. The Levenol solubilizing agents have a ready biodegradability higher than 60% which is the minimum required value according to OECD 301B measurement to be acceptably biodegradable.

Other polyesterified nonionic solubilizing agents also useful in the instant compositions are Crovol PK-40 and Crovol PK-70 manufactured by Croda GMBH of
15 the Netherlands. Crovol PK-40 is a polyoxyethylene (12) Palm Kernel Glyceride which has 12 EO groups. Crovol PK-70 which is preferred is a polyoxyethylene (45) Palm Kernel Glyceride have 45 EO groups.

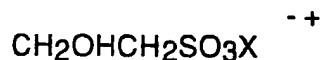
In the dilute o/w microemulsion compositions or liquid crystal compositions the nonionic ethoxylated glycerol type solubilizing agent or the polyesterified nonionic
20 solubilizing agent will be present in admixture with the anionic detergent. The proportion of the nonionic ethoxylated glycerol type solubilizing agent or the polyesterified nonionic solubilizing agent based upon the weight of the liquid crystal composition or the final dilute o/w microemulsion composition will be 1.0% to 23%, more preferably 2.0% to 18%, most preferably 3% to 15% by weight.

25 All of the aforesaid ingredients in this light duty liquid detergent are water soluble or water dispersible and remain so during storage.

The resultant homogeneous liquid detergent exhibits the same or better foam performance, both as to initial foam volume and stability of foam in the presence of

soils, and cleaning efficacy as an anionic based light duty liquid detergent (LDLD) as shown in the following Examples.

The essential ingredients discussed above are solubilized in an aqueous medium comprising water and optionally, viscosity control agents such as alcohols and dihydroxy alcohols such as C₂-C₃ mono- and di-hydroxy alkanols, e.g. ethanol, isopropanol and propylene glycol. Suitable water soluble hydrotropic salts include sodium, potassium, ammonium and mono-, di- and triethanolammonium salts of C₁-C₃ substituted benzene sulfonates such as sodium xylene sulfonate or sodium cumene sulfonate. While the aqueous medium is primarily water, preferably said viscosity control agents are included in order to control the viscosity of the liquid composition and to control low temperature cloud clear properties. Usually, it is desirable to maintain clarity to a temperature in the range of 5°C to 10°C. Therefore, the proportion of viscosity control agent generally will be from 1% to 15%, preferably 2% to 12%, most preferably 3% to 8%, by weight of the detergent composition with the proportion of ethanol, when present, being 5% of weight or less in order to provide a composition having a flash point above 46°C. Preferably the viscosity control agent will be a mixture of ethanol and either sodium xylene sulfonate or sodium cumene sulfonate or a mixture of said sulfonates. Another extremely effective viscosity control agent used at a concentration of 0.1 to 5 wt. percent, more preferably 0.5 to 4.0 weight percent is isethionic acid or an alkali metal salt of isethionic acid having the formula:



wherein X is hydrogen or an alkali metal cation, preferably sodium.

In addition to the previously mentioned essential and optional constituents of the light duty liquid detergent, one may also employ normal and conventional adjuvants, provided they do not adversely affect the properties of the detergent. Thus, there may be used various coloring agents and perfumes; ultraviolet light absorbers such as the Uvinuls, which are products of GAF Corporation; sequestering agents such as ethylene diamine tetraacetates; magnesium sulfate heptahydrate; pearling

agents and opacifiers; pH modifiers; etc. The proportion of such adjuvant materials, in total will normally not exceed 15% of weight of the detergent composition, and the percentages of most of such individual components will be 0.1% to 5% by weight and preferably less than 2% by weight. Sodium formate can be included in the formula as a preservative at a concentration of 0.1 to 4.0%. Sodium bisulfite can be used as a color stabilizer at a concentration of 0.01 to 0.2 wt.%. Typical preservatives are dibromodicyano-butane, citric acid, benzylic alcohol and poly (hexamethylene-biguamide) hydro-chloride and mixtures thereof.

The instant compositions can contain 0 to 2.5 wt. %, more preferably 0.025 to 2.0 wt. %, most preferably 0.05 to 1.0 wt. % of an antibacterial agent. A preferred antibacterial agent is trichlorohydroxydiphenyl ether.

The instant compositions can contain 0.1 to 4 wt. %, more preferably 0.5 to 3.0 wt. % of an alkyl polysaccharide surfactant. The alkyl polysaccharides surfactants, which are used in conjunction with the aforementioned surfactant have a hydrophobic group containing from 8 to 20 carbon atoms, preferably from 10 to 16 carbon atoms, most preferably from 12 to 14 carbon atoms, and polysaccharide hydrophilic group containing from 1.5 to 10, preferably from 1.5 to 4, most preferably from 1.6 to 2.7 saccharide units (e.g., galactoside, glucoside, fructoside, glucosyl, fructosyl; and/or galactosyl units). Mixtures of saccharide moieties may be used in the alkyl polysaccharide surfactants. The number x indicates the number of saccharide units in a particular alkyl polysaccharide surfactant. For a particular alkyl polysaccharide molecule x can only assume integral values. In any physical sample of alkyl polysaccharide surfactants there will be in general molecules having different x values. The physical sample can be characterized by the average value of x and this average value can assume non-integral values. In this specification the values of x are to be understood to be average values. The hydrophobic group (R) can be attached at the 2-, 3-, or 4- positions rather than at the 1-position, (thus giving e.g. a glucosyl or galactosyl as opposed to a glucoside or galactoside). However, attachment through the 1- position, i.e., glucosides, galactoside, fructosides, etc., is

preferred. In the preferred product the additional saccharide units are predominately attached to the previous saccharide unit's 2-position. Attachment through the 3-, 4-, and 6- positions can also occur. Optionally and less desirably there can be a polyalkoxide chain joining the hydrophobic moiety (R) and the polysaccharide chain.

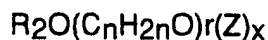
- 5 The preferred alkoxide moiety is ethoxide.

Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from 8 to 20, preferably from 10 to 18 carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkoxide chain can
10 contain up to 30, preferably less than 10, alkoxide moieties.

Suitable alkyl polysaccharides are decyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-
sides, galactosides, lactosides, fructosides, fructosyls, lactosyls, glucosyls and/or galactosyls and mixtures thereof.

- 15 The alkyl monosaccharides are relatively less soluble in water than the higher alkyl polysaccharides. When used in admixture with alkyl polysaccharides, the alkyl monosaccharides are solubilized to some extent. The use of alkyl monosaccharides in admixture with alkyl polysaccharides is a preferred mode of carrying out the invention. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-
20 sides and tallow alkyl tetra-, penta-, and hexagluco-
sides.

The preferred alkyl polysaccharides are alkyl polyglucosides having the formula



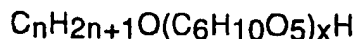
- wherein Z is derived from glucose, R is a hydrophobic group selected from the group
25 consisting of alkyl, alkylphenyl, hydroxyalkylphenyl, and mixtures thereof in which said alkyl groups contain from 10 to 18, preferably from 12 to 14 carbon atoms; n is 2 or 3 preferably 2, r is from 0 to 10, preferable 0; and x is from 1.5 to 8, preferably from 1.5 to 4, most preferably from 1.6 to 2.7. To prepare these compounds a long chain alcohol (R₂OH) can be reacted with glucose, in the presence of an acid catalyst to form the

desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (R_1OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (C_{1-6}) is reacted with glucose or a polyglucoside ($x=2$ to 4) to yield a short chain alkyl glucoside ($x=1$ to 4) which can in turn be reacted with a longer chain alcohol (R_2OH) to displace the short chain alcohol and obtain the desired alkyl polyglucoside. If this two step procedure is used, the short chain alkylglucoside content of the final alkyl polyglucoside material should be less than 50%, preferably less than 10%, more preferably less than 5%, most preferably 0% of the alkyl polyglucoside.

The amount of unreacted alcohol (the free fatty alcohol content) in the desired alkyl polysaccharide surfactant is preferably less than 2%, more preferably less than 0.5% by weight of the total of the alkyl polysaccharide. For some uses it is desirable to have the alkyl monosaccharide content less than 10%.

The used herein, "alkyl polysaccharide surfactant" is intended to represent both the preferred glucose and galactose derived surfactants and the less preferred alkyl polysaccharide surfactants. Throughout this specification, "alkyl polyglucoside" is used to include alkyl polyglycosides because the stereochemistry of the saccharide moiety is changed during the preparation reaction.

An especially preferred APG glycoside surfactant is APG 625 glycoside manufactured by the Henkel Corporation of Ambler, PA. APG25 is a nonionic alkyl polyglycoside characterized by the formula:



wherein $n=10$ (2%); $n=12$ (65%); $n=14$ (21-28%); $n=16$ (4-8%) and $n=18$ (0.5%) and x (degree of polymerization) = 1.6. APG 625 has: a pH of 6 to 10 (10% of APG 625 in distilled water); a specific gravity at 25°C of 1.1 g/ml; a density at 25°C of 9.1 lbs/gallon; a calculated HLB of 12.1 and a Brookfield viscosity at 35°C, 21 spindle, 5-10 RPM of 3,000 to 7,000 cps.

The instant compositions can contain a silk derivative as part of the composition and generally constitute 0.01 to 3.0 % by weight, preferably 0.1 to 3.0% by weight, most preferably 0.2 to 2.5% by weight of the liquid detergent composition.

Included among the silk derivatives are silk fibers and hydrolyzate of silk fibers.

- 5 The silk fibers may be used in the form of powder in preparing the liquid detergent or as a powder of a product obtained by washing and treating the silk fibers with an acid. Preferably, silk fibers are used as a product obtained by hydrolysis with an acid, alkali or enzyme, as disclosed in Yoshiaki Abe et al., U.S. Patent No. 4,839,168; Taichi Watanube et al., U.S. Patent No. 5,009,813; and Marvin E. Goldberg, U.S. Patent No.
10 5,069,898, each incorporated herein by reference.

- Another silk derivative which may be employed in the composition of the present invention is protein obtained from degumming raw silk, as disclosed, for example, in Udo Hoppe et al., U.S. Patent No. 4,839,165, incorporated herein by reference. The principal protein obtained from the raw silk is sericin which has an
15 empirical formula of $C_{15}H_{25}O_3N_5$ and a molecular weight of 323.5.

Another example of a silk derivative for use in the liquid detergent composition of the present invention is a fine powder of silk fibroin in nonfibrous or particulate form, as disclosed in Kiyoshi Otoi et al., U.S. Patent No. 4,233,212, incorporated herein by reference.

- 20 The fine powder is produced by dissolving a degummed silk material in at least one solvent selected from, for example, an aqueous cupriethylene diamine solution, an aqueous ammoniacal solution of cupric hydroxide, an aqueous alkaline solution of cupric hydroxide and glycerol, an aqueous lithium bromide solution, an aqueous solution of the chloride, nitrate or thiocyanate of calcium, magnesium or zinc and an
25 aqueous sodium thiocyanate solution. The resulting fibroin solution is then dialyzed. The dialyzed aqueous silk fibroin solution, having a silk fibroin concentration of from 3 to 20% by weight, is subjected to at least one treatment for coagulating and precipitating the silk fibroin, such as, for example, by the addition of a coagulating salt,

by aeration, by coagulation at the isoelectric point, by exposure to ultrasonic waves, by agitation at high shear rate and the like.

The resulting product is a silk fibroin gel which may be incorporated directly into the liquid detergent composition or the same may be dehydrated and dried into a powder and then dissolved in the liquid detergent composition.

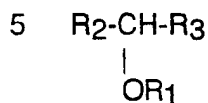
The silk material which may be used to form the silk fibroin includes cocoons, raw silk, waste cocoons, raw silk waste, silk fabric waste and the like. The silk material is degummed or freed from sericin by a conventional procedure such as, for example, by washing in warm water containing a surfact-active agent or an enzyme, and then dried. The degummed material is dissolved in the solvent and preheated to a temperature of from 60 to 95°C, preferably 70 to 85°C. Further details of the process of obtaining the silk fibroin are discussed in U.S. Patent No. 4,233,212.

A preferred silk derivative is a mixture of two or more individual amino acids which naturally occur in silk. The principal silk amino acids are glycine, alanine, serine and tyrosine.

A silk amino acid mixture resulting from the hydrolysis of silk of low molecular weight and having a specific gravity of at least 1 is produced by Croda, Inc. and sold under the trade name "CROSILK LIQUID" which typically has a solids content in the range of 27 to 31% by weight. Further details of the silk amino acid mixture can be found in Wendy W. Kim et al., U.S. Patent No. 4,906,460, incorporated herein by reference. A typical amino acid composition of "CROSILK LIQUID" is shown in the following Table .

AMINO ACID	PERCENT BY WEIGHT
Alanine	28.4
Glycine	34.7
Valine	2.0
Leucine	1.2
Proline	1.2
Tyrosine	0.6
Phenylalanine	0.9
Serine	15.4
Threonine	1.9
Arginine	1.5
Aspartic Acid	4.7
Glutamic Acid	4.1
Isoleucine	0.8
Lysine	1.4
Histidine	0.8
Cystine	0.1
Methionine	0.2
TOTAL	99.9

The instant compositions can also contain a supplemental viscosity modifying solvent at a concentration of 0.1 to 5.0 weight percent, more preferably 0.5 to 4.0 weight percent. The viscosity modifying agent is an alcohol of the formula



wherein $\text{R}_1 = \text{CH}_3, \text{CH}_2\text{CH}_3$

$\text{R}_2 = \text{CH}_3, \text{CH}_2\text{CH}_3$

$\text{R}_3 = \text{CH}_2\text{OH}, \text{CH}_2\text{CH}_2\text{OH};$

which is preferably 3-methyl-3-methoxy-butanol.

The 3-methyl-3-methoxy butanol is commercially available from Sattva Chemical Company of Stamford, Connecticut and Kuraray Co., Ltd., Osaka, Japan.

The instant composition can contain 0.1 to 4.0% of a protein selected from the group consisting of hydrolyzed animal collagen protein obtained by an enzymatic hydrolysis, lexeine protein, vegetal protein and hydrolyzed wheat protein and mixtures thereof.

The present light duty liquid detergents such as dishwashing liquids are readily made by simple mixing methods from readily available components which, on storage, do not adversely affect the entire composition. However, it is preferred that the nonionic surfactant, if present, be mixed with the viscosity control agent, e.g., ethanol and, if present, prior to the addition of the water to prevent possible gelation. The surfactant system is prepared by sequentially adding with agitation the anionic surfactant, the solubilizing agent which is a partially esterified ethoxylated polyhydric alcohol and the betaine to the nonionic surfactant which has been previously mixed with a viscosity control agent such as ethanol and/or sodium xylene sulfonate, and then adding with agitation the formula amount of water to form an aqueous solution of the surfactant system. The use of mild heating (up to 100°C.) assists in the solubilization of the surfactants. The viscosities are adjustable by changing the total percentage of active ingredients. No polymeric or clay thickening agent is added. In all such cases the composition made will be pourable from a relatively narrow mouth bottle (1.5 cm. diameter) or opening, and the viscosity of the detergent formulation will not be so low as to be like water. The viscosity of the composition desirably will be at least 100 centipoises (cps) at room temperature, but may be up to 1,000 centipoises as measured with a Brookfield Viscometer using a number 3 spindle rotating at 12 rpm. Its viscosity may approximate those of commercially acceptable products now on the market. The composition's viscosity and the composition itself remain stable on storage for lengthy periods of time, without color changes or settling out of any insoluble materials. The pH of this formation is substantially neutral to skin, e.g., 4.5 to 8 and preferably 5.5 to 5.0.

The preferred compositions of the instant invention are optically clear that is they exhibit a light transmission of at least 95%, more preferably at least 98%.

The instant microemulsion formulas explicitly exclude alkali metal silicates and alkali metal builders such as alkali metal polyphosphates, alkali metal carbonates, alkali metal phosphonates and alkali metal citrates because these materials, if used in

the instant composition, would cause the composition to have a high pH as well as leaving residue on the surface being cleaned.

These products have unexpectedly desirable properties. For example, the foam quality and deterative property is equal to or better than standard light duty liquid
 5 detergents while using a nonionic surfactant as the primary surfactant and minimal amounts of anionic surfactant, thereby achieving a mild, non-irritating liquid composition.

The following example is merely illustrative of the invention and is not to be construed as limiting thereof.

10

EXAMPLE 1

	A	B
NEODOL 91-9		13.5
NEODOL 1-9	8.5	
Cocoamidopropyl Betaine	5	4.8
Levenol F200	14.0	5
Linear Lauryl sulfonate (Sodium)	6.0	
Ammonium Lauryl Sulfonate		4.7
Sodium Formate		2
Formalin	0.1	--
C13-17 paraffin sulfonate		1.1
LMMEA		1.9
Sodium Bisulfite	0.05	0.05
Perfume	0.2	0.2
Water	Bal.	Bal.
Miniplate	13	28
Brookfield viscosity, RT, #2 spindle, 30 rpms (cps)	400	200

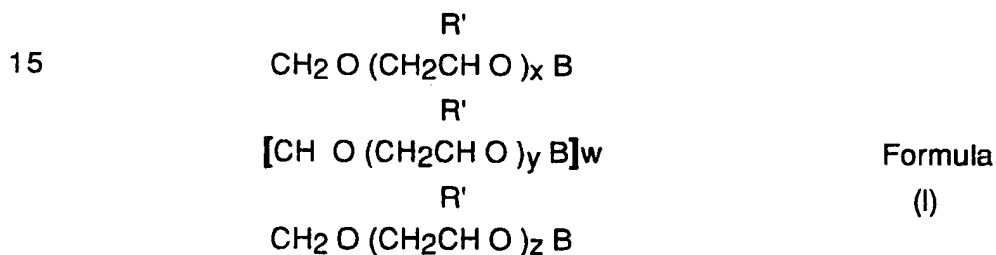
WHAT IS CLAIMED IS

1. A high foaming, light duty, liquid detergent comprising approximately, by weight:

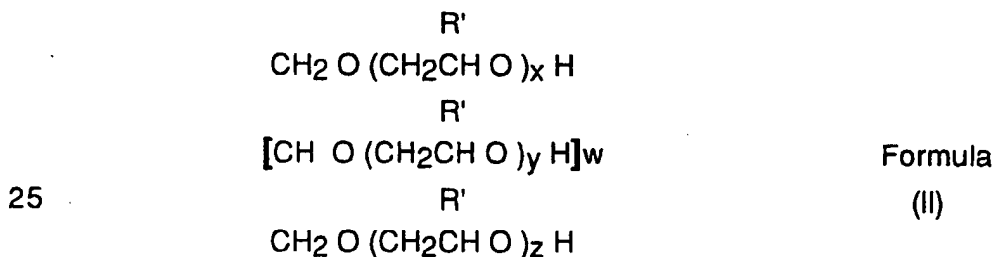
(a) 0% to 30% of a water soluble nonionic surfactant selected from the group consisting of primary and secondary C₈-C₁₈ alkanol condensates with 5 to 30 moles of ethylene oxide, condensates of C₈-C₁₈ alkylphenol with 5 to 30 moles of ethylene oxide;

(b) 0% to 40% of a water-soluble or water dispersible anionic surfactant selected from the group consisting of C₈-18 ethoxylated alkyl ether sulfate, C₈-C₁₈ alkyl sulfates, C₈-C₁₆ alkylbenzene sulfonates, C₁₀-C₂₀ paraffin sulfonates, C₁₀-C₂₄ alpha olefin sulfonates, C₈-C₁₈ alkyl sulfosuccinate esters, C₈-C₁₈ acyl isethionates and C₈-C₁₈ acyl taurates;

(c) 1% to 23% of a mixture of



20 and



wherein w equals one to four. B is selected from the group consisting of hydrogen or a group represented by:



wherein R is selected from the group consisting of alkyl group having 6 to 22 carbon atoms, and alkenyl groups having 6 to 22 carbon atoms, wherein at least one of the B groups is represented by said



and R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, provided that (x+y+z) equals 2 to 100, wherein in Formula (I) the ratio of monoester/diester/triester is 40 to 90/5 to 35/1 to 20, wherein the ratio of Formula (I) to Formula (II) is a value between 3 to 0.02;

- 10 (d) 0% to 10% of a water-soluble betaine; and
(e) balance being water, wherein said surfactants (a), (b) or (d) are present in an amount of at least 5 wt. % of said composition.

2. A liquid detergent composition according to claim 1 which includes, in addition, 1 to 15% by weight of a viscosity control agent selected from the group
15 consisting of C₂-C₃ mono- and di-hydroxy alkanols, water soluble alkali metal salts of C₁-C₃ substituted benzene sulfonate hydrotropes and mixtures thereof.

3. A liquid detergent composition according to Claim 2 wherein ethanol is present in the amount of 5% by weight or less.

4. A liquid detergent composition according to Claim 2 wherein said
20 nonionic surfactant is said condensate of a primary C₈-C₁₈ alkanol with 5-30 moles of ethylene oxide.

5. A liquid detergent composition according to Claim 4. wherein said anionic surfactant is selected from the group consisting of C₁₂-C₁₆ alkyl sulfates, C₁₀-C₁₅ alkylbenzene sulfonates, C₁₂-C₁₇ paraffin sulfonates and C₁₂-C₁₈ alpha
25 olefin sulfonates.

6. A liquid detergent composition according to Claim 1, wherein said nonionic surfactant is present in an amount of 1% to 25% by weight, said anionic surfactant is present in an amount of 1% to 30% by weight and said betaine is present in an amount of 1% to 9% by weight.

7. A liquid detergent composition, according to Claim 6 wherein said anionic detergent is a C₁₂-C₁₆ alkyl sulfate.
8. A liquid detergent composition according to Claim 1 further including a preservative.
- 5 9. A liquid detergent composition according to Claim 1 further including a color stabilizer.

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/us 95/02162

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D1/825 C11D1/83 C11D1/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 586 323 (KAO CORP.) 9 March 1994 cited in the application see the whole document ---	1-7
A	EP,A,0 573 341 (COLGATE PALMOLIVE CO.) 8 December 1993 see the whole document ---	1-9
A	US,A,4 595 526 (LAI KUO-YANN) 17 June 1986 cited in the application see the whole document ---	1-9
A	GB,A,1 453 385 (KAO SOAP CORP.) 20 October 1976 cited in the application see claims; example 4 ---	1,2
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "&" document member of the same patent family

Date of the actual completion of the international search

23 June 1995

Date of mailing of the international search report

28. 06. 95

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INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/us 95/02162

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	<p>DATABASE WPI Section Ch, Week 8403 Derwent Publications Ltd., London, GB; Class A97, AN 84-014343 & JP,A,58 206 693 (NIPPON EMULSION KK) , 1 December 1983 cited in the application see abstract ---</p>	1
A	<p>US,A,4 224 195 (KAWASAKI YOSHIMI ET AL.) 23 September 1980 cited in the application see claims; examples ---</p>	1,4,6
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A	<p>EP,A,0 535 693 (KAO CORP.) 7 April 1993 see claims ---</p>	1,4
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A	<p>US,A,3 928 251 (BOLICH JR. RAYMOND EDWARD ET AL.) 23 December 1975 see the whole document ---</p>	1,5
P,A	<p>EP,A,0 637 629 (COLGATE PALMOLIVE CO.) 8 February 1995 see claims -----</p>	1

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/02162

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